SYNTHESIS TEMPERATURE EFFECT ON THE STABILIZATION OF TETRAGONAL ZIRCONIA NANOPOWDERS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Ceramic Engineering

By
MD QANIT BIN TAKMEEL

Department of Ceramic Engineering
National Institute of Technology
Rourkela
2010

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Under the Guidance of
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CERTIFICATE

This is to certify that this thesis entitled, "SYNTHESIS TEMPERATURE EFFECT ON THE STABILIZATION OF TETRAGONAL ZIRCONIA NANOPOWDERS" submitted by Mr. Md Qanit Bin Takmeel in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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This report is the outcome of days of perseverance, evenings spent in the lab, nights spent reading journals, ecstasies on seeing some results, hear-tearing on seeing some other results, the occasional laughs and numerous discussions. However, there were other factors which are equally important in the successful presentation of this report.

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7th May, 2010 Md Qanit Bin Takmeel

CONTENTS

Abstract

The present work is an appraisal of the effectiveness of sodium borohydride in the stabilization tetragonal zirconia nanopowders, synthesized at different temperatures.

Zirconia ceramics have found broad applications in a variety of energy and biomedical applications because of their unusual combination of strength, fracture toughness, ionic conductivity, and low thermal conductivity. These attractive characteristics are largely associated with the stabilization of the tetragonal and cubic phases through alloying with aliovalent ions. The high fracture toughness exhibited by many of zirconia ceramics is attributed to the constraint of the tetragonal-to-monoclinic phase transformation and its release during crack propagation. In other zirconia ceramics containing the tetragonal phase, the high fracture toughness is associated with ferroelastic domain switching.

Our objectives in the present work include the preparation of zirconia nanopowders using sodium borohydride, the study of the effect of synthesis temperature on the properties of zirconia nanopowders, and the stabilization of tetragonal zirconia at room temperature.

In the first part of the work, the effect of temperature and solvent in the size reduction and hence stabilization of the tetragonal phase at room temperature was studied. It was revealed that with the increase in the synthesis temperature, the fraction of tetragonal phase in the calcined zirconia samples increased. Calcined powders at 700ºC were shown to exhibit as low as 11 nm particle size as revealed by TEM and BET specific surface area measurement. The fraction of tetragonal phase was inevitably linked to the particle or crystallite size: smaller crystallites were essential for the stabilization of t-ZrO_2 at room temperature.

The results of the first part of our work motivated us to carry on the stabilization of t-ZrO_2 with minimal amount of yttria as additive. The second part of the work dealt with the stabilization of zirconia in the presence of yttria. This stabilization is not possible because of the formation of yttrium orthoborate, as revealed by the X-Ray diffraction patterns, which separates out as a different phase, and prevents the stabilization of tetragonal zirconia.

Keywords: tetragonal zirconia (t-ZrO_2); sodium borohydride ($NaBH_4$); stabilization; nanocrystallites and nanopowders.

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Chapter 1

GENERAL INTRODUCTION

1.1 Introduction to zirconia

Zirconia is an important ceramic material and is used for a variety of applications. It has three polymorphic forms: monoclinic (<1170 ºC), tetragonal (1170 ºC-2370 ºC) and cubic (> 2370 ºC). [1] [2]. The martensitic transformation (t-ZrO_2 to m-ZrO_2) of zirconia leads to about 3% volume expansion, which may lead to catastrophic failure of the system [3]. Hence the use of Zirconia is limited. To increase its applicability, extensive work has been carried out, to retain the high temperature forms of zirconia at room temperature. Among the methods of stabilizing higher temperature forms of zirconia, the most common is the use of additives such as yttria[4], [5]. Other papers report the size reduction of the crystallites as an effective method to stabilize the higher temperature forms of zirconia.

1.2 Properties of zirconia

Zirconia has some unique properties such as high ionic conductivity [6], fracture toughness [7], strength [8] and low thermal conductivity [9]. These attractive properties are due to the stabilization of tetragonal and cubic phases at room temperature. Thus the need to investigate methods to stabilize higher temperature forms of zirconia at room temperature is of prime importance.

1.3 Major research on zirconia

Garvie [10] was the first to study and propose the critical size of the crystallite for tetragonal to monoclinic transformation. He also proposed a relation:

$$(G_t - G_m) + S_t\gamma_t \leq S_m\gamma_m$$

Where G is the molar free energy and S is the surface area in the single crystal particle. It was determined that particle size for stabilizing t- phase must be ≤ 30 nm. For cubic to tetragonal phase transformation, the critical crystallite size is about 2 nm. [11]

1.4 Applications of zirconia

These properties of zirconia have found a large number of engineering applications. Stabilized c-ZrO_2 and t-ZrO_2 has special applications as oxygen sensors, determination of pollutant gases and high temperature solid oxide fuel cells (SOFC)[12-15]. Zirconia is used as a

dispersed phase in oxide (alumina) [16] as well as non-oxide (carbides, borides, and nitrides) [17] ceramics to increase their fracture toughness, strength, and hardness. Tetragonal ZrO_2 also finds application as catalyst/catalyst support for various gas-phase reactions [18-19]. Lately, the use of zirconia in bioceramic applications such as in dental prosthesis [20], bone replacement [21], bioceramic scaffolds [22] etc. has been estabilished.

1.5 Outline of the report

A brief introduction of the topic in hand is presented has been presented in this chapter. The next chapter deals with the available literature, and towards the end of the chapter, is mentioned the objectives and motivation of our work. Chapter 3 describes in detail the experimental procedures and the characterization techniques used. Chapter 4 discussed the results obtained, and seeks to provide and explanation to those results. The conclusions of the work are summarized in the final chapter, and along with it, is provided some hints to future work.

Chapter 2

LITERATURE REVIEW

2.1 Stabilization of tetragonal and cubic zirconia nanopowders

The interest in stabilization of tetragonal and cubic zirconia at room temperature is gaining popularity, due to its excellent thermal stability, chemical resistance, mechanical properties and oxygen conductivity [2]. Stabilization depends on the type and amount of stabilizing agent, particle size and heat treatment temperatures.

Controlled addition of stabilizing oxides such as yttria, magnesia, ceria and rare earth oxides may retain high temperature phase at room temperature. [23]

Stabilization of metastable phases depends on the crystallite size [24-25] and process of powder preparation. [26].

M. Rezaei et. al [27] have investigated the several process parameters such as the type of zirconium precursor, pH value, refluxing time, refluxing temperature and surfactant to zirconium molar ratio on the structural properties of the powders.

Ultrafine powders of ZrO_2-Y_2O_3 solid solutions have been synthesized by hydrothermal treatment and have been reported extensively in literature. Zirconia gel, crystalline Y_2O_3 and various mineralizing solutions have been utilized as precursors for the hydrothermal synthesis. Yttria-stabilized zirconia (YSZ) with different Y_2O_3 content and characterized by different crystallite sizes have been produced by changing the hydrothermal treatment temperature, and the nature and concentration of the mineralizer solution [28-29]

It has been established that the stabilization of the metastable tetragonal phase in nanocrystalline zirconia is the result of the minimization of surface energy. [1]

Different routes (such as chemical precipitation, hydrothermal, gas-condensation, sonochemical, and sol–gel processes) are employed for the synthesis of stabilized *t*- or *c*-ZrO_2 with controlled particle size and morphology [30-34]

Literature is abundant with methods dealing with the synthesis of zirconia nanopowders from the sol-gel route [35-36**]** and hydrothermal routes [37]. For hydrothermal route, various precipitating reagents are used. The most common among them are ammonium hydroxide [6] and hydrazine hydride [38]. But very few papers have dealt with the synthesis of zirconia nanopowders by using a stronger reducing agent such as sodium borohydride. [39]

When tetragonal to monoclinic transformation occurs, it is called a Martensitic transformation, and is accompanied by a 3-5 vol% expansion which may result in material

fracture [3]. Thus, the need to stabilize higher temperature forms of zirconia at room temperature arises.

If alcohol-aqueous mixture is used, the stabilization of higher temperature forms of zirconia at room temperature becomes more benign [40].

For cubic to tetragonal phase transformation, the critical crystallite size is about 2 nm [11] and Garvie [10] was the first to determine the critical crystallite size of tetragonal zirconia for it to transform to the monoclinic phase.

Using high-resolution transmission electron microscopy Satyajit Shukla et al [41] estabilished that "hard-aggregates" forming tendency of ZrO_2 nanocrystallites of size ~45 nm is responsible for stabilizing the high temperature metastable tetragonal phase, at room temperature, within large sized (500-600 nm) undoped ZrO_2 particles.

It was demonstrated by Xin Guo et al. [42] that the water molecules are incorporated into the ZrO_2 lattice during annealing, and the amount of the incorporated water is determined by the water vapor pressure. Owing to the filling of oxygen vacancies by the incorporated water molecules, part of the tetragonal ZrO_2 transformed to the monoclinic structure, and protonic defects were induced. The expected proton conduction was confirmed by the polarity of the water vapor concentration cells.

The kinetic studies of the reactions between sodium borohydride and methanol, water and their mixtures have been studied extensively, between -20ºC and 50ºC. It has been found that hydrogen generation rate follows 1^{st} order kinetics with respect to sodium borohydride concentration and methanolysis of sodium borohydride can generate hydrogen at low temperatures [43]

Nanocrystalline ZrB_2 powders have been prepared by the reaction of $ZrCl_4$ with $NaBH_4$ in the temperature range of 500 °C–700 °C. The microstructure of the powders consists of uniform particles about 20 nm in size. [44]

2.2 Summary of Literature

The following is the gist of the literature survey:

(a) Various routes have been employed to synthesize tetragonal zirconia nanopowders.

(b) In order to stabilize tetragonal zirconia, additives are used.

(c) However, reducing the crystallite size of zirconia is one way of stabilizing the tetragonal phase at room temperature, without the addition of stabilizers.

(d) Among the various routes for zirconia nanopowders synthesis, sol-gel route and hydrolysis route are the most common, and have yielded sufficiently small crystallites to stabilize the tetragonal phase up to 500 ºC.

(e) When hydrothermal route has been employed, high pH of the precipitate is shown to yield higher fraction of tetragonal zirconia.

(f) The studies pertaining to the use of sodium borohydride for the synthesis of zirconia have not been extensive; however, the reagent has been used to synthesize other compounds such as zirconium boride which shows promise in its use for the synthesis of zirconia.

(g) The kinetic studies of sodium borohydride have shown that with the increase in temperature, the rate of dissociation of sodium borohydride to form hydrogen increases.

2.3 Objectives of the present studies

Since very little work has been reported in literature regarding the synthesis of zirconia nanopowders using sodium borohydride as a precipitating reagent, the present work seeks to deal with the following:

(a) Synthesis of zirconia nanopowders using sodium borohydride as the precipitating reagent.

(b) Study of the effect of synthesis temperature on the properties of zirconia nanopowders, as the kinetics of sodium borohydride varies with temperature.

(c) Study of the effect of synthesis temperature on the properties of zirconia nanopowders when ammonium hydroxide is used as the precipitating agent, to compare the results.

(d) Study of the effect of additives on the properties of zirconia nanopowders when sodium borohydride is used as a precipitating reagent.

Chapter 3

EXPERIMENTAL WORK

3.1 Synthesis of pure Zirconia

3.1.1 Experimental Setup

0.5M zirconium oxychloride (pH 0.3) solution (with water and 10% methanol separately) was taken in a beaker and placed on a heater cum magnetic stirrer. To achieve the desired reaction temperature (0ºC, 25ºC and 80ºC), the beaker was either cooled or heated using an ice bath or heater. 0.5 M sodium borohydride (pH 11) was added drop-wise into the zirconium oxychloride solution until a gel formed which then dissolved to form a precipitate of pH 9.

3.1.2 Powder Preparation

The precipitate was left overnight at room temperature and subsequently, washed several times till the pH dropped down to 7. The sample was placed in an oven at 50ºC for drying. The dried samples were ground and calcined at 600ºC for 1 hour and 700ºC for 1 hour. The nomenclature of the powder samples (sample identification) thus obtained shall consist of the following:

1. The first alphabet shall represent the solvent used. 'W' stands for distilled water and 'M' stands for 10% methanol.
2. The second alphabet stands for the precipitating reagent used. 'B' stands for sodium borohydride and 'N' stands for ammonium hydroxide.
3. The next two numbers represent the synthesis temperature of the sample in the Celsius scale.
4. 'c' represents calcination, and the number following that, multiplied by 100 would give the calcination temperature of the samples. Since, the soaking time, during heat treatment was 1 hour; it is not represented in the sample identification.

Thus WB80-c07 would mean that the sample was prepared using water as the solvent, the precipitating reagent used was sodium borohydride, the synthesis temperature was 80ºC and the sample was calcined for 1 hour at 700ºC.

3.1.3 Powder Characterization

The differential scanning calorimetry and thermogravimetric analysis was carried out in (NETZCH, Germany). Samples were analysed with a heating rate of 10ºC/min in the temperature range 30ºC to 900ºC. Nitrogen physisorption was used to determine the surface area of the materials at the temperature of liquid nitrogen (-196ºC) in a (Quantachrome, USA); prior to analysis the samples were degasified for 2 hours at 180ºC. X-Ray diffraction patterns were obtained in a PANalytical (model number) diffractometer with a Cu K_α radiation (λ=0.15406 nm) with a graphite secondary beam monochromator; the intensities of the diffraction beam were obtained in the 2θ range between 20º and 80º and a measuring time of 20 minutes. To obtain the microstructure of the samples, the powders were subjected to Transmission Electron Microscopy. Debye-Scherer formula was used to determine the crystallite size.

3.2 Synthesis of yttrium doped zirconia

3.2.1 Experimental Setup

Desired amount of yttria was taken; nitric acid was added, heated till a clear solution was obtained indicating the conversion of yttria to yttrium nitrate. This was added to 0.5M zirconium oxychloride (pH 0.3) solution (with water and 10% methanol separately) taken in a beaker and placed on a heater cum magnetic stirrer. To achieve the desired reaction temperature, the beaker was either cooled or heated using an ice bath or heater. 0.5 M sodium borohydride (pH 11) was added drop-wise into the zirconium oxychloride solution until a gel formed which then dissolved to form a precipitate. The final pH of the solution was kept at 9.

3.2.2 Powder Preparation

The precipitate was left overnight at room temperature and subsequently, washed several times till the pH dropped down to 7. The sample was placed in an oven at 50 ºC for drying. The dried samples were ground and calcined at 700 ºC, 800 ºC and 1200 ºC for 1 hour. The nomenclature of the powder samples (sample identification) thus obtained shall consist of the following:

1. The first two numbers followed by Y divided by 10 shall represent the percentage of yttria in the sample.

2. The second alphabet shall represent the solvent used. ‘W’ stands for distilled water and ‘M’ stands for 10% methanol.
3. The third alphabet stands for the precipitating reagent used. ‘B’ stands for sodium borohydride and ‘N’ stands for ammonium hydroxide.
4. The next two numbers represent the synthesis temperature of the sample in the Celsius scale.
5. ‘c’ represents calcination, and the number following that, multiplied by 100 would give the calcination temperature of the samples. Since, the soaking time, during heat treatment was 1 hour; it is not represented in the sample identification.

Thus 05YWB80-c08 would mean that the sample has 0.5% Yttria, was prepared using water as the solvent, the precipitating reagent used was sodium borohydride, the synthesis temperature was 80ºC and the sample was calcined for 1 hour at 800ºC.

3.2.3 Powder Characterization

X-Ray diffraction patterns were obtained in a PANalytical (model number PW 3040) diffractometer with a Cu K_α radiation (λ=0.15406 nm) with a graphite secondary beam monochromator; the intensities of the diffraction beam were obtained in the 2θ range between 20º and 80º and a measuring time of 20 minutes. Debye-Scherer relation was used to determine the crystallite size.

Chapter 4

RESULTS AND DISCUSSION

4.1 Introduction

The first part of this section deals with the thermal, structural, microstructural and BET surface area characterization of the pure zirconia nanopowders synthesized. The second part deals with the structural characterization of zirconia powders prepared in the presence of yttrium oxide.

4.2 Characterization of pure zirconia

4.2.1 Thermal

Figures 4.1 (a), (b) and (c) show the DSC-TG profiles of as-prepared zirconia powders, synthesized at 0 ºC, 25 ºC and 80 ºC using $NaBH_4$ respectively.

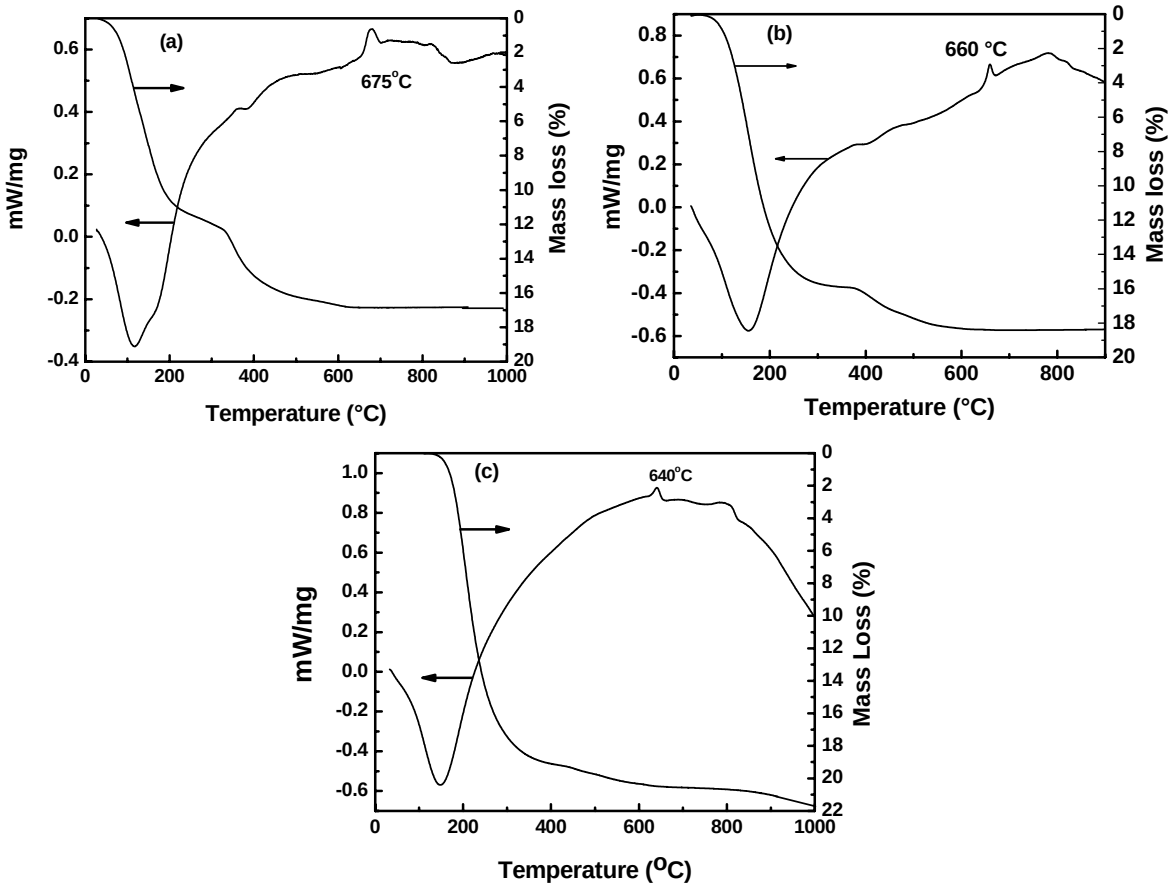

Fig 4.1: DSC-TG of (a) WB00 (b) WB25 (c) WB80

The figures show an endothermic peak accompanied by weight loss in the temperature region 150 °C- 200 °C when the zirconia powders were synthesized using $NaBH_4$. This peak was due to loss of water of crystallization or physically absorbed water. [26].

At about 370 ºC-400 ºC, there a small endothermic peak accompanied by a sudden weight loss was observed. With the increase in the temperature of synthesis, the intensity of the aforementioned peak decreased.

An exothermic peak was observed in the temperature zone 640 ºC-680 ºC. This exothermic peak was not accompanied by any weight loss. This peak was due to a change in phase and possibly due to the conversion of the amorphous zirconia phase to the tetragonal zirconia. [26] It is also observed that this temperature of conversion decreases as the synthesis temperature was increased.

At ~790 °C, an exothermic peak was observed which was due to the transformation of tetragonal zirconia to monoclinic zirconia. [27], [45]

In addition, a DSC-TGA was performed on an unwashed sample (Fig.4). It can be seen that the DSC curve has serrations from 300 ºC to 500 ºC and a distinct endothermic peak at 805ºC. These may be due to the melting of B_2O_3 (which melts over a range of temperature between 250ºC and 500ºC) and NaCl (melting point 805ºC). Based on this, the following reaction can be proposed.

$$ZrOCl_2.8H_2O + NaBH_4 \rightarrow Zr(OH)_4.nH_2O + B_2O_3 + NaCl \quad (1)$$

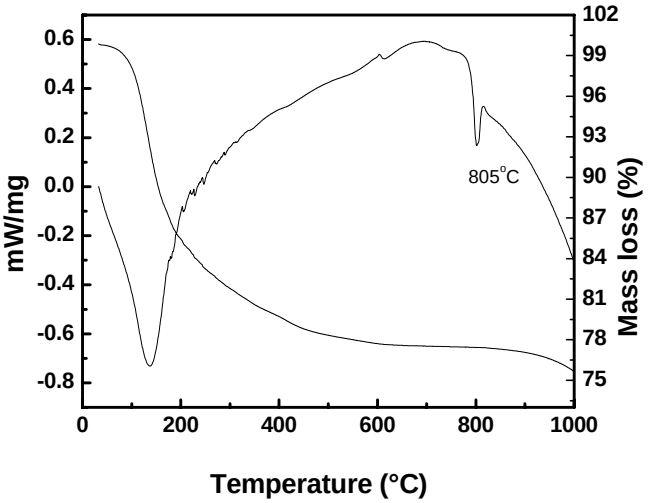

Figure 4.2 DSC-TG of unwashed sample

DSC-TG showed that although the onset transformation of amorphous zirconia to tetragonal zirconia was earlier at higher synthesis temperatures, the complete transformation took a longer time. To substantiate these results, the as-prepared powders were calcined at various temperatures and their XRD patterns were analyzed.

4.2.2 Structure and microstructure

Figures 4.3 (a), (b), (c) and (d) show the XRD patterns of zirconia powders prepared by altering various synthesis parameters and calcined at various temperatures.

XRD patterns were used to identify the various phases and the crystallite sizes of the samples. Figure 4.3 (a) shows the XRD patterns of zirconia samples synthesized at different temperatures with $NaBH_4$ as the precipitating reagent and calcined at 600ºC. The pattern suggests that the phase in all the three cases is tetragonal. It was seen that with the decrease in synthesis temperature, the peaks appeared to be broader, indicating that the crystallinity had increased [46-48]. This is in agreement with the DSC-TG data, which showed that the onset of the conversion of the amorphous to tetragonal phase started early with the increase in synthesis temperature, because of the early removal of chemically bonded water.

Figure 4.3 (b) shows the XRD patterns of zirconia samples synthesized at different temperatures with $NaBH_4$ as the precipitating reagent and calcined at 700ºC. The pattern shows that the fraction of tetragonal phase increases at higher temperatures of synthesis, and at a synthesis temperature of 80 ºC the phase is 100% tetragonal. This, again, is in agreement with the DSC-TG curves, which show that the increase in the synthesis temperature results in the broadening of the amorphous to tetragonal phase peaks, which leads to a delay in the conversion of the tetragonal to the monoclinic phase.

Figure 4.3 (c) shows the XRD patterns of zirconia samples synthesized at different temperatures with NH_4OH as the precipitating agent and calcined at 700ºC. The pattern shows that with a change in synthesis temperature, there was no significant change in the fraction of tetragonal phase in the calcined samples. This suggests that the effect of temperature in the stabilization of higher temperature phases of zirconia at room temperature was seen only when the precipitating reagent was $NaBH_4$.

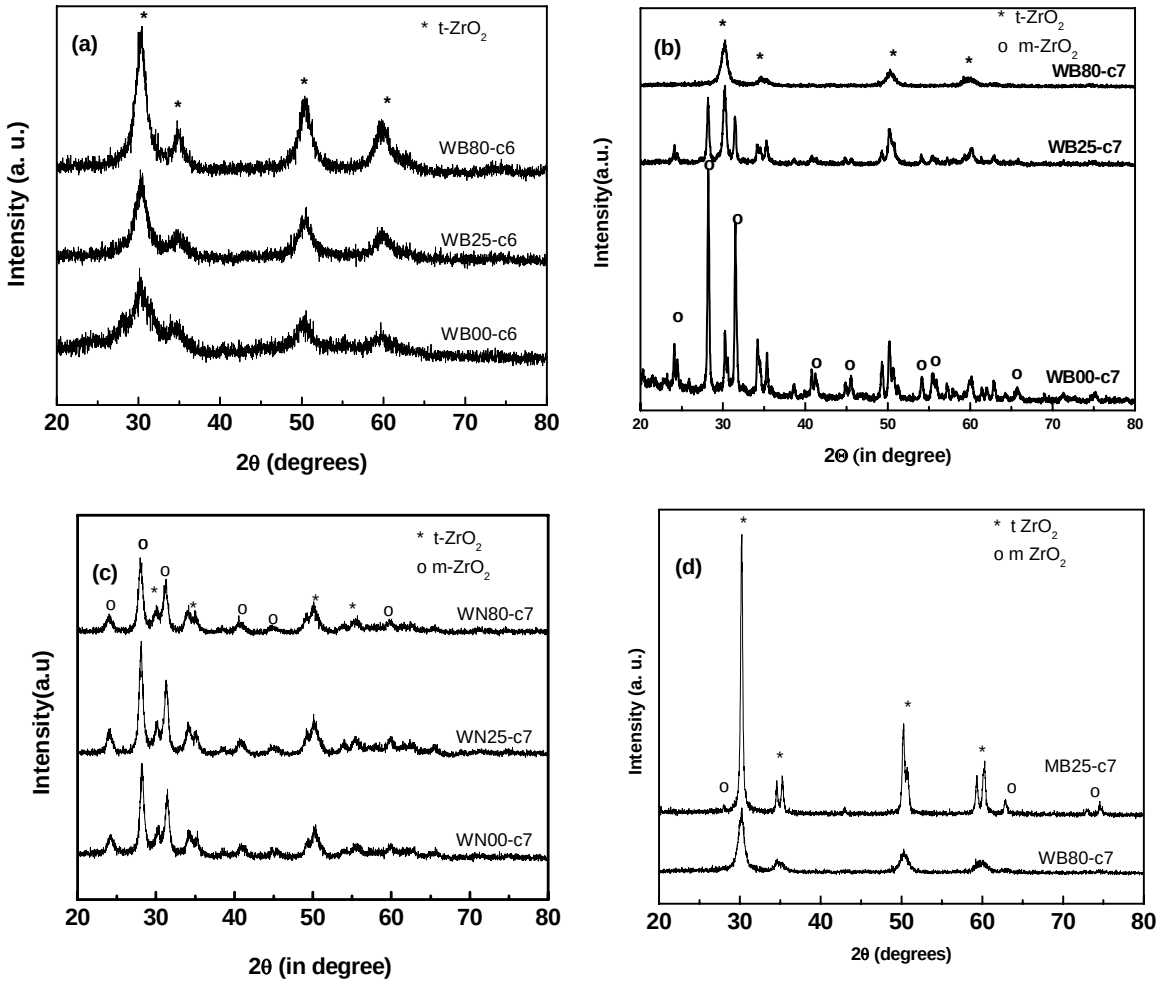

Fig. 4.3: XRD patterns of ZrO_2 prepared using (a) water as solvent and $NaBH_4$ as precipitating reagent at various synthesis temperatures, calcined at 600ºC; (b) water as solvent and $NaBH_4$ as precipitating reagent at various synthesis temperatures, calcined at 700ºC; (c) water as solvent and NH_4OH as precipitating reagent at various synthesis temperatures, calcined at 700ºC and (d) different solvents and $NaBH_4$ as precipitating reagent calcined at 700ºC

We used a different solvent, methanol. $NaBH_4$ when dissolved in methanol at room temperature. The resulting XRD pattern of zirconia samples prepared by $NaBH_4$ with methanol as the solvent and calcined at 700ºC is shown in figure 4.3(d) and for comparison, the XRD pattern of zirconia sample prepared at 80ºC, with $NaBH_4$ with water as solvent and calcined at 700ºC is given. It is seen that both the patterns show nearly 100% tetragonal phases.

Figures 4.4(a) and 4.4(b) show The TEM micrographs of WB80-c7 sample. The TEM micrographs of the WB80-c7 samples reveal that the particles are elongated and have a particle size of about 10 nm. This elongation appears to be due to the clustering of two or three spherical

particles, to form an ellipsoidal structure. Figure 4.4 (a) also shows that the nanopowders have a mesoporous structure.

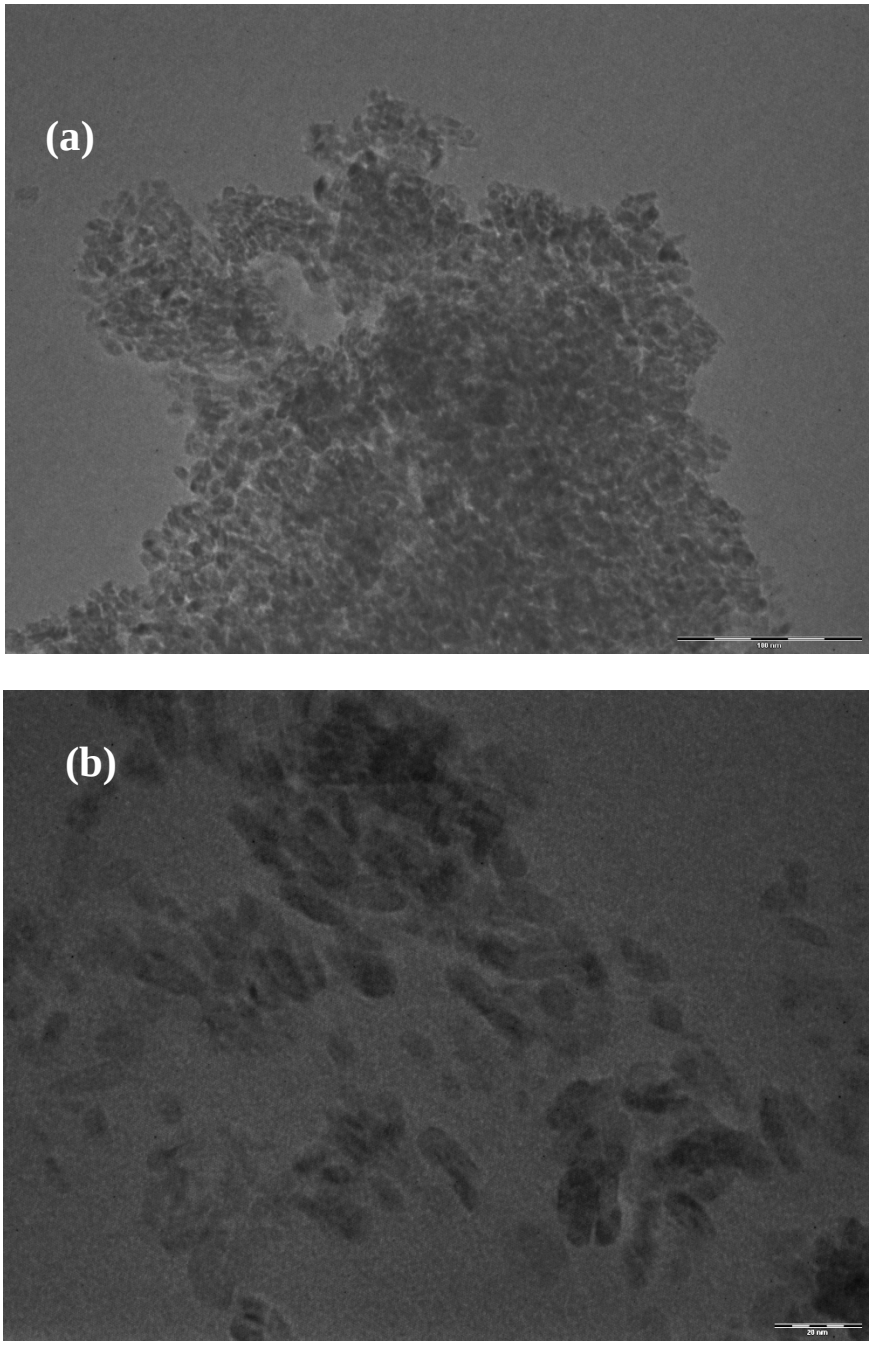

Fig 4.4 (a) TEM micrographs of WB80-c7 with 100 nm resolution (b) TEM micrograph of WB80-c7 with 20 nm resolution.

4.2.3 Surface Area

The surface area of the sample was determined using Brunauer-Emmett-Teller (BET). The measured surface area was converted to equivalent particle size according to the equation:

$$D_{BET} = \frac{6000}{\rho \times S_{BET}} \quad (2)$$

where, D_{BET} (nm) is the average particle size, S_{BET} is the surface area expressed in $m^2.g^{-1}$ and ρ is the theoretical density of t-ZrO_2 expressed in $g.cm^{-3}$.

The specific surface area of WB80-c7 is about 7.5 times more than the specific surface area of WB00-c7.

Table 4.1: Major and minor phases from XRD, crystallite size, surface area from BET and particle size from BET

Sample	Major phase	Minor phase	Crystallite size (nm)	BET surface area (m^2/g)	Particle size from BET surface area (nm)
WB00-c6	t-ZrO_2	-	1.63	-	-
WB25-c6	t-ZrO_2	-	3.38	-	-
WB80-c6	t-ZrO_2	-	3.65	-	-
WB00-c7	m-ZrO_2	t-ZrO_2,	36.54	7.494	133.44
WB25-c7	t-ZrO_2,	m-ZrO_2	30.55	-	-
WB80-c7	t-ZrO_2,	m-ZrO_2	11.11	58.29	17.16
WN00-c7	m-ZrO_2	t-ZrO_2,	10.50	-	-
WN25-c7	m-ZrO_2	t-ZrO_2,	17.34	-	-
WN80-c7	m-ZrO_2	t-ZrO_2,	13.05	-	-
MB25-c7	t-ZrO_2		61.11	-	-

4.2.4 Remarks

The increase in synthesis temperature during the preparation of zirconia nanopowders using $NaBH_4$ plays an important role in the stabilization of the tetragonal phase at room temperature. This is due to the size reduction of the crystallites.

The results above are motivating enough to carry on further studies, on the stabilization of t-ZrO_2 by the addition of yttria, which is the most commonly used additive for the purpose. The results of the tests are dealt with in the following section.

4.3 Characterization of yttria added zirconia nanopowders

4.3.1 Structure

Figures 4.5 (a), (b) and (c) show the XRD patterns of various Y_2O_3 added zirconia systems. It can be seen that 100% tetragonal phase has not been achieved for any sample.

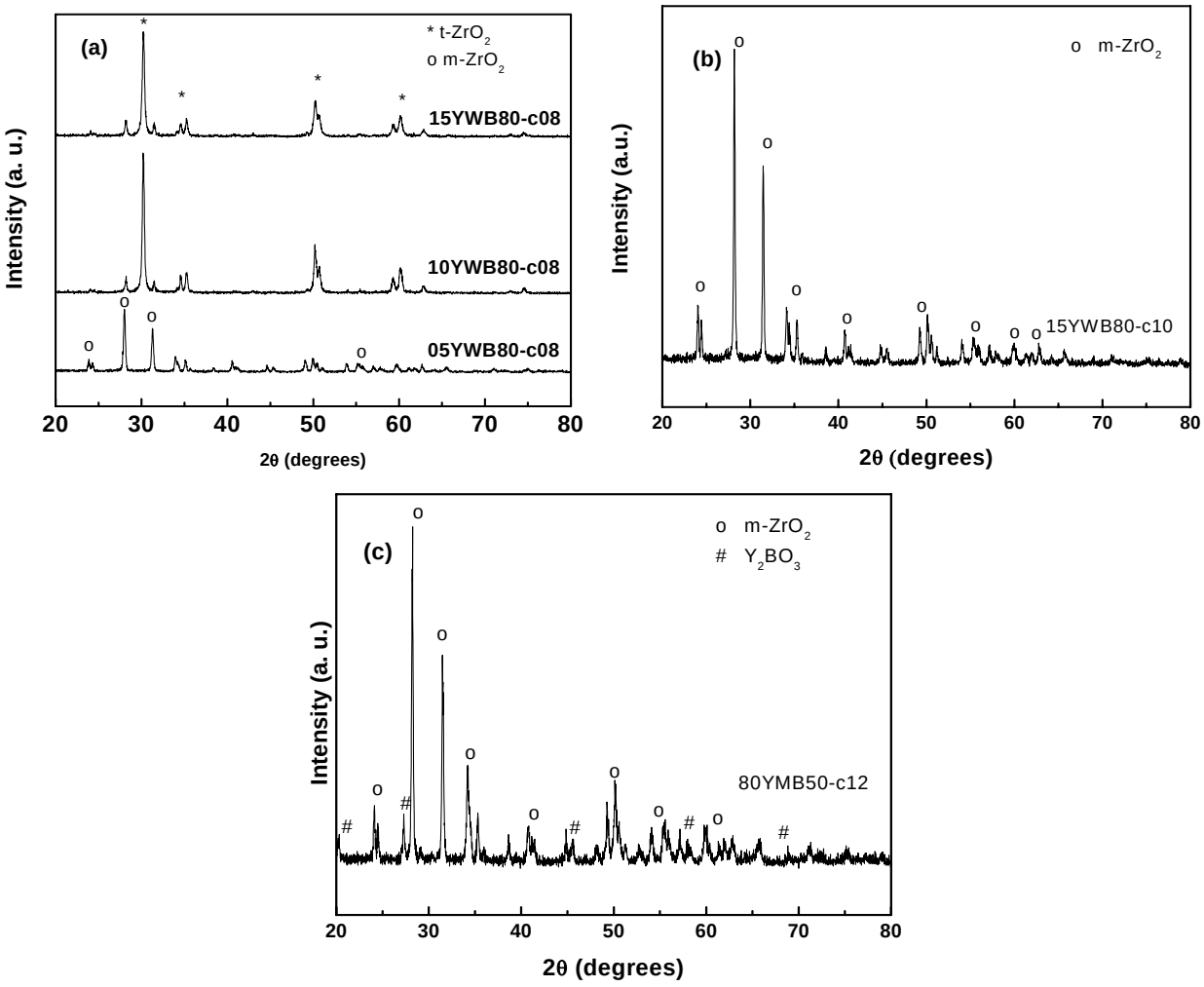

Fig 4.5: XRD patterns of (a) varying Y_2O_3-ZrO_2 system when synthesized at synthesis temperature 80ºC with $NaBH_4$ as the precipitating reagent, water as solvent and calcined at 800ºC; (b) 1.5% Y_2O_3-ZrO_2 system when synthesized at synthesis temperature 80ºC with $NaBH_4$ as the precipitating reagent, water as solvent and calcined at 1000ºC and (c) 8% Y_2O_3-ZrO_2 system when synthesized at synthesis temperature 50ºC with $NaBH_4$ as the precipitating reagent, 10% methanol as solvent and calcined at 1200ºC.

Given the effectiveness of increased synthesis temperatures, it was sought to stabilize zirconia nanopowders with minimal amount of yttria. The XRD patterns of zirconia with varying percentages of yttria synthesized with $NaBH_4$ as the precipitating reagent at 80ºC and calcined at 800ºC are shown in figure 4.5 (a). At 0.5% Y_2O_3 the phase is completely monoclinic, but with increasing percentage of yttria, there is a greater fraction of tetragonal phase. Figure 4.5 (b) shows the XRD pattern of zirconia prepared with 1.5% yttria, using $NaBH_4$ calcined at 1000ºC for one hour. It shows that the phase is completely monoclinic.

In order to seek an explanation for this behavior, zirconia was prepared with 8% yttria with methanol as solvent and $NaBH_4$ as a precipitating reagent. The resultant powder was calcined at 1200ºC, and the XRD pattern of this sample is given in figure 4.5 (c). The presence of yttrium orthoborate phase is prominent in the pattern, which suggests that yttria does not form a solid solution with zirconia when synthesized with $NaBH_4$.

4.3.2 Remarks

Although $NaBH_4$ plays a major role in the stabilization of tetragonal phase at room temperature in pure zirconia powders, the reaction of $NaBH_4$ with yttrium ions results in the separation of a yttrium orthoborate phase, which prevents the stabilization of zirconia, by the addition of stabilizers. Thus, $NaBH_4$ is useful only in size reduction and its use in stabilizing the zirconia powders further, is limited.

Chapter 5

CONCLUSIONS

The findings of the present work are summarized below:

(1) The effect of synthesis temperature on the final phase of calcined zirconia powders were studied and it was found that for $NaBH_4$, higher synthesis temperatures resulted in greater fraction of metastable tetragonal phase. This effect of temperature was however, not observed when NH_4OH was used as the precipitating agent. The reason for this is the difference in mechanisms of the two reactions, the former occurring by reduction and the latter by hydrolysis.

(2) Crystallite size played a major role in the stabilization of the zirconia nanopowders. Smaller crystallites led to the stabilization of the tetragonal phase at room temperature. After calcination at 700 ºC, for one hour, crystallites of size as low as 11 nm were obtained.

(3) It was also ascertained that methanol, when used as a solvent with $NaBH_4$ is the precipitating reagent, is effective in the stabilization of tetragonal zirconia phase at room temperature.

(4) Despite the effectiveness of sodium borohydride as a precipitating reagent in the stabilization of tetragonal zirconia at room temperature, its use is limited when it is used to stabilize zirconia in the presence of yttria. This is because sodium borohydride reacts with yttrium salts to form yttrium orthoborate. Yttrium orthoborate separates out as a different phase and thus prevents yttrium ion to enter the lattice of zirconia structure, hence there is no stabilization.

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